ROLE OF STRONG ION EXCHANGE RESINS IN NITROSAMINE FORMATION IN WATER

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Abstract—N-Nitrosodimethylamine (NDMA) was formed when tap water was passed through a column containing only the anion exchange resin, thereby indicating that nitrosamine (NA) formation by the conventional acid catalyzed nitrosation reaction, as would be expected in the case of a mixed strong anion and cation resin system, was not the primary mechanism. The quaternary ammonium ion of the strong anion resin may be the amine precursor for NA formation. Strong anion and strong cation resins (Amberlite and Dowex brands‡) were ineffective in concentrationg low levels of NDMA that were added to the influent. Accumulation of extremely low levels of NA already present in the water, therefore, also did not contribute importantly to the concentration of NA found in deionized water. In addition, the normal levels of cations and anions in water, and heavy metal ions were also not primarily responsible for this occurrence. There was, however, an unknown substance(s) in tap water that promoted NA formation. This unknown soluble substance(s) can be removed by activated carbon treatment or degassing techniques.

INTRODUCTION

Ion exchange resins consist primarily of a polymer matrix and an ion-active group. The ion-active group is responsible for the ion exchange process, for example, the sulfonic acid for the strong cation, quaternary ammonium for the strong anion, carboxylic acid for the weak cation, and amines for the weak anion resins. The strong cation and anion resins, or a combination of these, are commonly used for water treatment. Deionization of water with ion exchange resins is used to produce water for high-pressure steam production, chemical and food processing, mining, agriculture, laboratory use, automobile battery water, in the home for steam irons; to a limited degree for drinking water in areas of high-salinity water and a variety of other areas (Wheaton & Seamster, 1966).

Nitrosamines (NAs) have been reported in deionized water by Fiddler et al. (1977), Cohen & Backman (1978), and Gough et al. (1977). N-Nitrosodimethylamine (NDMA) and -diethylamine (NDEA) have been confirmed in water exposed to deionizing resins by Fiddler et al. (1977). Levels of NDMA detected were 0.03–0.34 ppb, and for NDEA, 0.33 and 0.83 ppb. The highest levels of NAs were found after resin regeneration. NDMA levels of 0.25 ppb and lower concentrations were also detected in deionized water by Cohen & Backman (1978). The origin of the NAs in these reports was not identified. However,

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‡ Reference to brand or firm name does not constitute endorsement by the U.S. Department of Agriculture over others of a similar nature not mentioned.

Gough et al. (1977) suggested that NDMA present in the ion exchange resins (up to 125 μg kg^{-1}) as manufacturing contaminants, not the reaction of the components in the water with the resins, was responsible for the occurrence of trace levels of NDMA (0.01 ppb) detected in deionized water. NDMA was detected in the effluent when a 1 N NaNO$_2$ solution was passed through a mixed strong anion and cation resin column by Angeles et al. (1978). Formation of NDMA was postulated by the cation acid-catalyzed nitrosation of the amine/ammonium functional group on the strong anion resin during the deionization process.

The purpose of this investigation was to determine whether one of the explanations offered (Gough et al., 1977; Angeles et al., 1978) for the occurrence of NAs in water deionized with strong cation and anion resins is correct or whether some other factors are involved.

EXPERIMENTAL

Conditioning of resins

Some of the properties of the strong Dowex (Dow Chemical, Midland, MI) and Amberlite (Rohm and Haas, Philadelphia, PA) brand resins (suitable for deionization of water) that were used in this investigation are shown in Table 1. Polystyrene was the matrix for all of the resins; the diameter of the particles was 20–50 mesh (840–297 μ).

Unused water-swollen resins were conditioned prior to use with 1 N HCl and 1 N NaOH and washed with distilled or deionized water after each treatment with the acid or base solution until the effluent was neutral to litmus paper (Duolite Ion Exchange Manual, 1966). The resins were then regenerated to the H$^+$ or OH$^-$ ion form with 1 N HCl (cation resin) or 1 N NaOH (anion resin).

Extraction of nitrosamines

Aqueous solutions. One litre (Table 2), in two portions, or 0.5 l. (Tables 3–9) of an aqueous solution was extracted

Table 1. Some of the properties of strong anion and cation resins

Resin	Chemical classification	Functional group	Ion form	Capacity, total (meq/ml (wet))	Moisture content (%)
Dowex 1-X8	Strong-base anion (type I)	Trimethyl-benzyl ammonium	Cl^-	1.33	39–45
Dowex 2-X4	Strong-base anion (type II)	Dimethyl-ethanol-benzyl ammonium	Cl^-	1.2	54–60
Dowex 21K	Strong-base anion (type I)	Trimethyl-benzyl ammonium	Cl^-	1.25	54–60
Dowex 50W-X8	Strong-acid cation	Sulfonic acid	H^+	1.7	53
Amberlite IR-120	Strong-acid cation	Sulfonic acid	H^+	1.75	52
Amberlite IRAK-401S	Strong-base anion (type I)	Trimethyl-benzyl ammonium	Cl^-	0.80	59–65

with 3 × 150 ml portions of dichloromethane (DCM; Burdick & Jackson, Muskegan, MI) with shaking for 5 min per extraction. The DCM extracts were combined, dried over anhydrous Na_2SO_4, and concentrated in a Kuderna–Danish evaporator to 1.0 ml. When 250 ng each of NDMA and N-nitrosopyrrolidine were added to 0.5 l. of distilled water and the mixture was extracted by the above procedure, recovery of NAs was 90% or greater.

Resins. Water-swollen ion exchange resins (c. 100 g or 200 ml) were placed in a flask with 3 × 150 ml DCM, and the flask was stoppered and shaken vigorously for 5 min. The DCM extracts were decanted into an Erlenmeyer flask containing anhydrous Na_2SO_4 and concentrated by the procedure described above.

Ability of resins to retain N-nitrosodimethylamine

After being conditioned, the Amberlite or Dowex resins were extracted with DCM. The resins were filtered under vacuum to remove DCM and stirred with water. The slurry was poured into 31 × 390 mm chromatographic columns, washed with deionized or distilled water, and regenerated with either 1 N HCl (cation) or 1 N NaOH (anion). The columns contained 200 ml wet volume of cation, anion, or mixed anion and cation resins. The influent consisted of 500 ml distilled water containing 50 μl NDMA standard (5 ng μl^{-1} in DCM). This was followed by 1.0 l. of distilled water at a flow rate of 1 bed vol·h^{-1}. The resulting effluent was extracted with DCM. The resins in the columns were allowed to stand overnight, then were filtered and washed with distilled water. The filtrate (400 ml) was extracted with DCM. Extraction of the resins and the workup of the final extracts were as described previously.

Nitrosamine formation on resin column

Two 34 × 580 mm glass tubes were used as columns for the mixed resins. The influent was applied to the column via the separatory funnel. The flow was adjusted at the bottom with a piece of Tygon tubing equipped with a screw clamp. A 31 × 390 mm chromatographic column was used for the strong anion resins. The mixed resins contained 200 or 270 ml wet vol. of 1:1.5 (v/v) mixture of Dowex 50W-X8 in the H^+ form, and Dowex 21K in the Cl^- form, and 230 ml of a 1:2 (v/v) mixture of Amberlite IR-120 in the H^+ form, and Amberlite IRA-401S in the Cl^- form.

The conductance of the effluent was measured by a Heathkit voltmeter, with copper wire electrodes kept at a fixed distance from each other. When the resins were exhausted, the column was backwashed to separate the mixed resins into two layers. The cation resin was located at the bottom of the column. The separated resins were physically removed, then packed in 31 × 390 mm chromatographic columns and regenerated with 1.0 l. of 1 N HCl (cation) or 1 N NaOH (anion) over a period of 1 h, followed by distilled water (c. 10 bed vol·h^{-1}) until the effluent was neutral to litmus paper.

For a given influent, the last 500 ml of effluent was analyzed when one analysis was performed, whereas for multiple analyses, 500 ml of effluent was analyzed at regular intervals.

Influents used

1. *Municipal (tap) water.* The Philadelphia Surburban Water Company supplies the water at the Center. Analyses by the water company were as follows: pH = 7.5; alkalinity, 146; hardness, 236 mg l^{-1}; chlorine, c. 0.6 to 0.8 ppm during the winter and 1.0 to 1.5 ppm during the summer; heavy metal ion when detected, Fe, 0.01 to 0.03 ppm. Cu ion was also detected but this was due to the oxidation of the copper from the copper-containing pipes and fixtures. Tap water was analyzed for Nas. N-Nitrosohexamethylenimine (NHMI; 100 ng) was dissolved in 1.0 l. of tap water as an internal standard; 500 ml was extracted with DCM, and 100 ppm Na_2SO_3 was added to the remaining 500 ml and allowed to stand 30 min prior to extraction with DCM. Recovery of NHMI was greater than 90%.

2. *Tap water passed through Filtrasorb* 400 *column.* Tap water at the rate of 6–7 bed vol·h^{-1} was passed through a 31 × 390 mm column containing 200 ml of Filtrasorb 400 (Calgon Corp., Pittsburgh, PA). This activated carbon was extracted with DCM to remove NAs that may have been contaminants from its manufacture, air dried, and finally dried in an oven at 110°C prior to use. Activated carbon has been shown to remove NAs from water (Borneff, 1978).

3. *Degassed tap water.* Tap water was placed in an Erlenmeyer flask, and argon gas was bubbled through for 1 h with stirring at a brisk flow rate.

4. *Principal anion solution.* To simulate the influent containing the principal anions at average concentrations found in the tap water at the Center, 0.63 ml of 0.5 M Na_2SO_4, 4.6 ml 0.5 M $NaHCO_3$ and 1.68 ml 0.5 M NaCl solutions were added to sufficient distilled water to prepare 1.0 l. of solution. This was equivalent to 30 ppm SO_4^{2-}, 140 ppm HCO_3^- and 30 ppm Cl^-.

5. *Principal cation solution.* For the corresponding cation levels, 2.0 ml 0.5 M $CaCl_2$, 1.66 ml 0.5 M $MgCl_2$, and 1.3 ml 0.5 M NaCl solutions were added to distilled water to prepare 1.0 l. of solution equivalent to 40 pp. Ca^{2+}, 20 ppm Mg^{2+} and 15 ppm Na^+.

6. *Metal ion solutions.* Three solutions containing 1,000 ppm with respect to the metal ion were prepared in 1.0-l. volumetric flasks with the following quantities of reagent grade inorganic compounds: (a) 2.28 g $3CdSO_4·8H_2O$ (Alfa Products, Beverly, MA), 4.05 g $NiCl_2·4H_2O$ (Baker Chemical, Phillipsburg, NJ), 3.10 g $Ce(NO_3)_3·6H_2O$ (Baker), 3.60 g $MnCl_2·4H_2O$ (Baker), 2.69 g $CuCl_2·2H_2O$ (Baker) and 4.40 g $ZnSO_4·7H_2O$

(Mallinkrodt Chemical, St. Louis, MO). (b) 1.35 g $HgCl_2$ (Baker), and 4.85 g $FeCl_3 \cdot 6H_2O$ (Baker). (c) 2.95 g $SnCl_4 \cdot 5H_2O$ (Baker). One milliliter from each of the three solutions was added per 1. of tap water after passage through the Filtrasorb 400 column.

7. *Chlorine containing solution.* A gallon of bleaching agent (Clorox) was purchased from a local supermarket. This solution contained 5.25% NaOCl or 2.5% (25,000 ppm) chlorine. For the determination of NAs content of the influent, 1.0 l. of a solution of 100 ng NHMI (internal standard), 0.5 ml Clorox (12.5 ppm), and tap water treated with Filtrasorb 400 was left standing for 4 h, and then 200 ppm Na_2SO_3 was added. After standing for an additional 30 and 60 min, 500 ml portions were extracted with DCM. NAs were not detected, and the recovery of added NHMI was greater than 90%.

8. *Solution containing nitrogen oxides.* Nitric oxide, generated by the reaction of 1 M $NaNO_2$ with 1 M ascorbic acid at a pH of 3.5, was bubbled into a 1.01 l. separatory funnel containing distilled water until c. 500 ml of water was displaced; the funnel was stoppered, shaken, then opened to to the atmosphere and shaken. The resulting brownish gas readily dissolved in the water. This procedure was repeated until the gases in the separatory funnel no longer dissolved in the water. The reaction of O_2 and NO is instantaneous, and the resulting oxides of nitrogen hydrolyze in water to give nitrite and nitrate (Mellor, 1940). The level of the oxides of nitrogen remaining in this solution was unknown; the odor of NO_2 was readily detectable in this solution.

9. *Amine solution.* Diethylamine (DEA) and triethylamine (TEA) were used as their hydrochloride derivatives. The NA content of the influent was determined as follows: One l. of a solution containing 2.7 ppm DEA, 100 ng NHMI (internal standard) and tap water or tap water that was passed through the Filtrasorb 400 column was allowed to stand 4 h. Then 500 ml was extracted with DCM; 100 ppm Na_2SO_3 was added to the remaining 500 ml, which was then allowed to stand for an additional 30 min prior to extraction with DCM. Recovery of NHMI was greater then 90% for all of the samples.

Analysis of nitrite

The nitrite level of tap water before and after treatment with Filtrasorb 400 was determined by the Griess colorimetric method (Fiddler, 1977).

Analysis of amines

A gas chromatograph equipped with a nitrogen-phosphorus detector (Model 5710A, Hewlett–Packard, Avondale, PA) and a 1.8 m $\times$ 2 mm i.d. glass column packed with Carbopack B/4% Carbowax 20 M/0.8% KOH (Supelco, Bellefonte, PA) was used. The flow rates were: He, 20 ml min^{-1}; H_2, 3.5 ml min^{-1}; and air, 80 ml min^{-1}. The injector and detector temperatures used were 200 and 250°C, respectively. The column was programmed from 70 to 150°C at 4° min^{-1} and held at the upper temperature for 4 additional min. Then 2 μl samples were injected. Standard solutions of diethylamine and triethylamine were at a concentration of 1 ppm.

Analysis of nitrosamines

Samples (7–8 μl) from 1.0 ml concentrates of DCM extracts were injected into a Model 2700 Varian-Aerograph, (Varian Assoc., Palo Alto, CA) gas–liquid chromatograph interfaced with a Model 502 Thermal Energy Analyzer (TEA; Thermo Electron, Waltham, Mass.). A 2.7 m $\times$ 0.5 mm Ni column tubing (Alltech Assoc., Arlington Heights, IL) was packed with 15% Carbowax 20 M-TEA on 60–80 Gas Chrom P. The GLC operating conditions were: injector temperature, 200°C; He flow rate, 40 ml min^{-1}; column temperature programmed from 130 to 220°C or 110 to 210°C at 4°C min^{-1}. The TEA conditions were similar to those that have been reported (Fine & Rounbehler, 1975). Chromatographic peaks obtained from the samples were compared with those from standard NAs for their precise retention times and quantitation.

Extracts containing apparent NAs were sealed in melting point capillary tubes and subjected to u.v. light at 365 nm for 1–2 h (Doerr & Fiddler, 1977). These samples were again subjected to GLC-TEA to determine if the photolabile NAs disappeared.

GLC–mass spectrometric analysis

For the confirmation of the identity of the NAs, a Varian Aerograph Model 2700 gas chromatograph equipped with a 1.8 m $\times$ 2 mm i.d. glass column packed with 15% Carbowax 20 M-TPA on 60–80 Gas Chrom P was connected to a Varian MAT 311A (Varian Assoc., Florham Park, NJ) mass spectrometer. The helium flow rate was 15 ml min^{-1}. The temperatures used were: detector, 200°C; injector port, 200°C; GLC–mass spectrometer interface system, 180°C; and column programmed from 90 to 130°C at 4° min^{-1} for

Table 2. Ability of strong cation and anion resins to retain NDMA*†

| Resin | NDMA recovered‡, % of total | | | % Total |
	Effluent	Filtrate	Resin	NDMA recovered
Dowex 50W-X8, H⁺ form	85	ND‖	ND	85
Dowex 21K, OH⁻ form	87	4	2	93
Dowex 50W-X8, H⁺ form plus Dowex 21K, OH⁻ form	85	2	1	85
500 ml influent plus 500 ml distilled water	—	—	—	85
Amberlite IR-120, H⁺ form	80	ND	ND	80
Amberlite IRA-401S, OH⁻ form	69	ND	1	70
Amberlite IR-120, H⁺ form plus Amberlite IRA-401S, OH⁻ form	87	ND	ND	87
500 ml influent plus 500 ml distilled water	—	—	—	79

* 200 ml wet v of resin.
† Flow rate, 1 bed v h^{-1}.
‡ 250 ng NDMA added.
§ Resin filtered and washed; 400 ml.
‖ Not detected; <1%.

Table 3. Nitrosamine formation on mixed strong anion (Dowex 21K) and strong cation (Dowex 50W-X8) resin column*; effect of tap water before and after treatment with Filtrasorb 400 activated carbon

Experiment	Influent	Influent† (l)	NDMA in effluent (ppb)
1	Tap water	5	1.26‡
		4	1.77‡
		6	2.03‡
	Resins separated and regenerated; regenerated cation resin placed on top of regenerated anion resin.		
2	Tap water		
	No treatment	2	0.24§
	Filtrasorb 400 treatment	2	0.002
	No treatment	4	1.57§
	Filtrasorb 400 treatment	3	0.006

* 200 ml wet v.
† Flow rate, c. 5 bed v h⁻¹.
‡§ Combined and confirmed by MS.

NDMA and NDEA. The mass spectrometer was operated in the peak matching mode adjusted to a resolution of 1 in 10,000 or 12,000. The mass spectra were obtained at an ionizing voltage of 70 eV and an ion source temperature of 150°C. The mass-to-charge ratios (m/e of 74.04799) for NDMA and (m/e of 102.07930) for NDEA were determined with the m/e 69.99857 and m/e 99.99361 perfluorokerosene reference peaks, respectively, by measuring the difference in m/e. The signal was recorded on an oscilloscope and a recording oscillograph.

Some of the representative samples containing NAs as determined by GLC-TEA were combined and checked by mass spectrometry. Generally, NA concentrations of 5 ng μl^{-1} or greater, injected, could be confirmed by this method.

RESULTS AND DISCUSSION

Investigations on ion-exchange resins

With the exception of Dowex 2 strong anion resin, the unused resins used in this investigation were extracted with DCM to determine their NA content. NDMA and NDEA at levels of 0.02–0.04 μg kg⁻¹ were detected in two of nine resin samples.

NAs present in the resin as manufacturing contaminants have been postulated as the source of the 0.01 ppb NDMA detected in deionized water (Gough et al., 1977). The possibility of this occurrence as the source of the NAs reported in the deionized water at the Center (Fiddler et al., 1977) was investigated indirectly. Distilled water spiked with NDMA was passed through the resins and NDMA retention was determined (Table 2); 6% was the highest retention found. If NAs were present as contaminants in the resins as a result of manufacturing conditions they would be expected to wash out after several deionization–regeneration cycles. Since strong anion and cation resins do not significantly retain NDMA, they also would not be expected to concentrate trace amounts of NA that may be found in tap water as contaminants.

NDMA levels of 1.26–2.03 ppb were detected in the effluent when tap water was passed through a new Dowex mixed bed of strong cation and anion resins (Table 3). Tap water was not the source of NDMA, since none was detected in the water prior to resin treatment. The resins were separated, regenerated, and the cation was placed on top of the anion resin. NDMA levels similar to the mixed resins were obtained when tap water was passed through the column; however, when the tap water was pretreated with Filtrasorb 400 granular activated carbon, NDMA was reduced to trace levels. It appears, therefore, that an unknown precursor or promoting agent (PA) was present in municipal water that was responsible for the concentration of NDMA found. The PA was not an amine or metal cation which would have been removed by the cation resin.

Dowex 2 and Dowex 1, both in the OH⁻ form, yielded results that were similar to those for the Dowex mixed resins. These results (Table 4) show that the cation resin is not needed for NA formation, thus indicating that the reaction is not cation acid-catalyzed, as has been postulated (Angeles et al., 1978). When tap water was boiled gently for 5 min it also produced low levels of NDMA similar to that achieved with activated carbon, suggesting that the PA in tap water is a gas, a volatile material, or a heat sensitive substance.

Effect of anions and cations

A mixed bed column was treated with tap water until the resins became exhausted, i.e. when the conductance of the effluent increased by c. 0.4 μmhos. The conductance of deionized water was generally 3.3 μmhos and that for tap water 200 μmhos. The exhausted resins were regenerated between each treatment; therefore, each deionization to exhaustion then regeneration represented one cycle. Table 5 shows the results obtained when the tap water treated with Filtrasorb 400, or distilled water containing 2–3 times the average amount of the principal anions or cations

Triethylamine produced no enhancement of NDEA formation. NDEA levels of 0.73–1.39 ppb were detected when a mixture of 2.7 ppm DEA in tap water was extracted with DCM after Na_2SO_3 was added to reduce residual chlorine without exposure to the ion exchange resins. Therefore, with added DEA in the influent, an enhancement of NDEA formation was due to reaction of DEA and tap water. When DEA was added to Filtrasorb 400 treated tap water and then passed through the resin column (data not shown in Table 8) no enhancement of NDEA was observed. In the presence of amines, chlorine has been shown to form NAs when the aqueous mixture was extracted with DCM; however, NA was absent when the residual chlorine was reduced with stoichiometric quantities of Na_2SO_3 prior to extraction with DCM (Logsdon et al., 1977). Thus extracts of the tap water containing added 2.7 ppm DEA but no added Na_2SO_3 contained 60–80% greater levels of NDEA than did those containing Na_2SO_3. When 2.7 ppm DEA was added to Filtrasorb 400 treated tap water, NDEA levels were less than 0.02 ppb, indicating that a NA forming reactant was removed from tap water by the activated carbon. Nitrite was not the primary factor, since the $NaNO_2$ level was identical for the tap water before and after treatment with Filtrasorb 400 (less than 60 ppb). Chlorine was a factor, since the addition of 0.5 ppm chlorine and 2.7 ppm DEA to Filtrasorb 400 treated tap water, with Na_2SO_3 added prior to DCM extraction, resulted in the detection of 1.1 ppb NDEA.

In a related experiment not shown on Table 8, NDEA was not detected; however, NDMA levels of 0.38–2.60 ppb were detected in the effluent after tap water was passed through a column containing 8 mg DEA added to the regenerated cation resin prior to mixing the regenerated cation and anion resins. Since the fate of DEA, whether added to the influent or the resin, will be similar, i.e. both will be protonated by the H^+ of the cation resin, the above results also suggest that NDEA formation on the resin column will be minor when DEA is present in the influent. The 5.5 mg DEA recovered from the added 8 mg in the effluent from the regenerated cation resin was greater than the 0.5 mg trimethylamine (primary decomposition product of the Type I strong anion resin) found, or the 1 and 1.4 mg recovered from the effluent of the regenerated cation resins from Cycles 1 and 2, respectively, from Table 8. Since the conditions for NA formation will be more favorable with a secondary amine (such as DEA) compared to a tertiary amine (such as trimethylamine), trimethylamine is not expected to be the amine precursor for NA formation on the resin column. The amine precursor for NDMA is thought to be the strong anion resin. If trimethylamine is not the amine precursor, then the quaternary ammonium ion of the anion resin is suggested to be the amine precursor. Quaternary methylammonium compounds have been shown to be precursors for NDMA (Fiddler et al., 1972).

Trace organic impurities which remain after resin manufacture will not be completely removed by the resin conditioning procedure used. A solvent extraction procedure (Junk et al., 1974) was used to eliminate these trace impurities in the resin. Subsequent passage of tap water through a column containing

Table 9. Nitrosamine formation on mixed strong anion (Dowex 21K) and strong cation (Dowex 50W-X8) resin column*; effect of chlorine, oxygen, and nitrogen oxides

Cycle†	Influent	Influent‡ (l)	NDMA in effluent (ppd)
1	Tap water	4	0.92
	Tap water degassed with argon (TDA)	3	0.006
	TDA + 200 ml oxides of nitrogen soln. + 2.5 ppm chlorine	3	0.006
	TDA + 0.8 ppm chlorine	3	0.049
	TDA + 2.5 ppm chlorine	3	0.169
	TDA + 5 ppm chlorine	3	0.348§
	TDA + 10 ppm chlorine	3	0.69§
2	Tap water	2	0.84¶
	TF** + 190 ml oxides of nitrogen soln. + 0.8 ppm chlorine	3	0.007
	TF‖ + 190 ml oxides of nitrogen soln. + 2.5 ppm chlorine	3	0.008
	Tap water	2	0.93¶
	TF aerated with O_2 for 1 h, + 0.8 ppm chlorine	3	0.197‖
	TF + 0.8 ppm chlorine	3	0.133‖
	TF	2	0.015

* 270 ml wet v of resins.
† Equivalent to deionization until exhaustion, then regeneration between each treatment.
‡ Flow rate, 3.0 to 3.7 bed v h^{-1}.
§‖ Combined and confirmed by MS.
¶ Confirmed by MS.
** Tap water treated with Filtrasorb 400.

this solvent extracted resin (Dowex 21K in the OH⁻ form) resulted in NDMA levels (0.08–0.32 ppb) similar to that found from an untreated resin column. This indicated that trace organic impurities in the resin were not NA precursors.

Effect of chlorine

The addition of chlorine to tap water degassed with argon enhanced NDMA formation on the mixed Dowex resin column (Table 9). Increasing the chlorine level increased NDMA formation. The Philadelphia Surburban Water Company has reported that the chlorine content of the finished water leaving the treatment plant varies from 0.6 to 1.5 ppm. Chlorine alone, therefore, does not seem to be the PA. Tap water will be expected to contain oxygen and perhaps oxides of nitrogen. Therefore the effect of oxides of nitrogen and chlorine, and chlorine and oxygen on NA formation during passage through the resin column was investigated. Oxides of nitrogen obtained by the reaction of $NO + O_2$ will hydrolyze to give nitrite and nitrate. Dissolved oxides of nitrogen values in water is not known. Nitrite formed by the hydrolysis of the nitrogen oxides may reduce added chlorine; however, the fate of the added chlorine is unknown. The mixture of oxides of nitrogen solution and chlorine showed no enhancement of NDMA formation. Chlorine and a combination of chlorine and oxygen enhanced NDMA formation, but this was less than the NDMA levels normally obtained with tap water. Numerous experiments in which chlorine and a combination of chlorine and oxygen were added to the influent were variable (Kimoto, unpublished), and the apparent difference shown in Table 9 (0.133 and 0.197 ppb for chlorine and chlorine + oxygen, respectively) was not considered significant.

GENERAL DISCUSSION

The Center's deionization system of sand or gravel, activated carbon, and mixed strong anion and cation resin beds, which had been used for an unknown number of years, were replaced with new materials prior to the start of this project. With these new deionization materials, NDMA was not detected in the deionized water. The present results suggest that a decrease in the efficiency of the carbon bed due to age and exhaustion was responsible for the level of NAs found in the Center's deionized water (Fiddler et al., 1977). The carbon bed was probably only partially effective in removing the unknown promoting agent from tap water.

Note: Precautions should be exercised in the handling of nitrosamines, since they are potential carcinogens.

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Table 4. Nitrosamine formation on strong anion (Dowex 1 and Dowex 2) resin columns; Effect of Tap water before and after treatment with Filtrasorb 400 activated carbon

Influent	Influent† (l)	Dowex 2 (Type II)* NDMA detected in effluent (ppb)
Tap water		
No treatment	5	4.36‡
Filtrasorb 400 treatment	3	ND‖
No treatment	2	7.16‡
Boiled gently for 5 min	2.75	0.004
		Dowex 1 (Type 1)¶
Tap water		
No treatment	4	0.64§
Filtrasorb 400 treatment	3	0.003
No treatment	3	1.11§

* 130 ml wet v.
† Flow rate, 5.8–8.7 bed v h^{-1}.
‡§ Combined and confirmed by MS.
‖ Not detected, <0.002 ppb.
¶ 145 ml wet v.

found in tap water, was spiked with 30 ppm $NaNO_2$, then passed through a mixed Dowex brand resin column. The highest level of NDMA found was 0.066 ppb, and the next highest was 0.025 ppb, when the influent was distilled water containing the cations Mg^{2+}, Ca^{2+}, and Na^+, suggesting a slight enhancement due to these cations.

With the Dowex mixed strong anion and cation resins, the highest level of NDMA found was 0.01 ppb with Filtrasorb 400 treated tap water spiked with 30 and 1–30 ppm $NaNO_2$ (Tables 5 and 6).

Effect of heavy metal ions

A number of heavy metal ions added to tap water treated with Filtrasorb 400 did not significantly enhance NDMA formation when the water was passed through the Dowex or Amberlite mixed resin column (Table 7). When untreated tap water was again passed through the column, however, enhance-

ment of NDMA formation demonstrated that the resin column was functioning normally. Lower levels of NDMA were again found when the heavy metal ion-containing influent was then passed through the column. These results indicated that the PA was not a heavy metal ion. The level of metal ions used was much higher than normally expected to be present in tap water.

Effect of added diethylamine and triethylamine

The strong cation resin or the mixed resins will retain amines by protonation as indicated by Table 8. When diethylamine (DEA), added to tap water, was passed through the mixed resin column, the level of DEA in the effluent was similar to the level found in tap water. Most of the added DEA was found in the effluent during the regeneration of the cation resin (greater than 85%). Triethylamine did not appear to be retained by the cation resin as efficiently as DEA.

Table 5. Nitrosamine formation on mixed strong anion (Dowex 21K) and strong cation (Dowex 50W-X8) resin column*; effect of anion and cations

Cycle†	Influent (all with added 30 ppm $NaNO_2$)	Influent‡ (l)	NDMA in effluent (ppb)	No. of analyses
	Tap water—Filtrasorb 400 treated			
1	No added cations or anions	20	ND§	3
2	No added cations or anions	20	0.003–0.005	3
	Distilled water (ppm) plus:			
3	60 SO_4^{2-}, 280 HCO_3^-, 60 Cl^-	10	ND	2
4	90 SO_4^{2-}, 420 HCO_3^-, 90 Cl^-	6	0.004	2
5	60 Mg^{2+}, 120 Ca^{2+}, 45 Na^+	6	0.025, 0.066	2
6	40 Mg^{2+}, 80 Ca^{2+}, 30 Na^+	10	0.015, 0.023	2
7	305 Cl^-	5	0.009	1
	60 SO_4^{2-}, 280 HCO_3^-, 60 Cl^-	5	0.017	1

* 270 ml wet v.
† Equivalent to deionization until exhaustion, then regeneration between each treatment.
‡ Flow rate, 3.1–3.8 bed v h^{-1}.
§ Not detected, <0.002 ppb.

Table 6. Nitrosamine formation on mixed strong anion (Dowex 21K) and strong cation (Dowex 50W-X8) resin column*; effect of added $NaNO_2$

Cycle[†]	Influent	Influent[‡] (l)	NDMA in effluent (ppb)	No. of analyses
	Tap water—Filtrasorb 400 treated plus			
1	1 ppm $NaNO_2$	22	ND[§] − 0.004	4
2	1 ppm $NaNO_2$	19.5	ND	3
3	5 ppm $NaNO_2$	18	ND	3
4	10 ppm $NaNO_2$	18	ND	3
5	20 ppm $NaNO_2$	18	ND − 0.010	3
6	30 ppm $NaNO_2$	18	ND − 0.006	3

* 200 ml wet v.
[†] Equivalent to deionization until exhaustion, then regeneration between each treatment.
[‡] Flow rate, 4.6–5.3 bed v h^{-1}.
[§] Not detected, <0.002 ppb.

Table 7. Nitrosamine formation on strong anion and strong cation mixed resin column; effect of metal ions

Cycle[‡]	Tap water influent treatment	Dowex 21K + 50W-X8*			Amberlite IRA-401S + IR-120[†]		
		Influent[§] (l)	NDMA in effluent (ppb)	No. of analyses	Influent[‖] (l)	NDMA in effluent (ppb)	No. of analyses
1	Filtrasorb 400[¶]	9	0.003, 0.004	2	6	0.003	1
	None	2	0.128**	1	3	0.37[††]	1
	Filtrasorb 400[¶]	9	0.005, 0.007	2	9	0.004	2
2	Filtrasorb 400[¶]	8	0.002	2	6	0.005	1
	None	4	0.77**	1	3	0.44[††]	1
	Filtrasorb 400[¶]	8	0.006, 0.008	2	9	0.003	2

* 270 ml wet v.
[†] 230 ml wet v.
[‡] Equivalent to deionization until exhaustion, then regeneration between each treatment.
[§] Flow rate, 3.2–3.7 bed v h^{-1}.
[‖] Flow rate, 3.8–4.0 bed v h^{-1}.
[¶] 30 ppm $NaNO_2$, and 1 ppm of added: Cd^{2+}, Ni^{2+}, Ce^{3+}, Mn^{2+}, Cu^{2+}, Zn^{2+}, Hg^{2+}, Fe^{3+}, Sn^{4+} ions.
**,[††] Combined and confirmed by MS.

Table 8. Nitrosamine formation on mixed strong anion (Dowex 21K) and strong cation (Dowex 50W-X8) resin column*; effect of Diethylamine (DEA) and Triethylamine (TEA)

Cycle[†]	Influent	Influent[‡] (l)	Detected in effluent			
			NDMA (ppb)	NDEA (ppb)	DEA (ppm)	TEA (ppm)
1[§]	Tap water	5	2.00	ND[¶]	—	—
		3	4.67	ND	—	—
	Tap water + 2.7 ppm DEA	3	1.30[‖]	0.88[‖]	0.01	—
		5	2.80[‖]	1.37[‖]	0.02	—
		4	2.45[‖]	1.25[‖]	0.01	—
2**	Tap water	5	1.04	ND	0.03	0.05
	Tap water + 2.7 ppm DEA	3	1.44[††]	0.87[††]	0.02	0.07
	Tap water	3	6.1	0.013	0.02	0.03
	Tap water + 5 ppm TEA	3	4.7	0.006	0.02	3.5
	Tap water	3	3.77	0.002	0.03	0.04

* 200 ml wet v.
[†] Equivalent to deionization until exhaustion, then regeneration between each treatment.
[‡] Flow rate, 5.5–6.0 bed v h^{-1}.
[§] Residual $NaNO_2$ c. 28 mg.
[‖] Combined and confirmed by MS.
[¶] Not detected, <0.002 ppb.
** Residual $NaNO_2$ c. 11 mg after anion resin was regenerated.
[††] Confirmed by MS.